

LOW TEMPERATURE PHYSICS

FOUR LECTURES

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by

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FOREWORD

THE FOUR LECTURES printed in this volume constituted a course given at the Royal Institution in the February and March of 1950. The form and contents of the lectures have been substantially retained, but they have been revised here and there to include some of the more recent developments.

We hope that this volume may not only serve as an introduction to the subject for young physicists who intend to specialize in low temperature physics, but also as a general survey of the field for those whose interest in it is less direct.

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LOW TEMPERATURE PROBLEMS, A GENERAL SURVEY

by F. E. SIMON

MY AIM TO-DAY is to introduce a course of lectures dealing with Low Temperature Physics, which is now one of the most flourishing parts of modern science. In doing so I want to discuss a few of its general features, and to tell you why this region near the absolute zero excites our attention; a region, incidentally, in which man has considerably surpassed Nature herself.

To get the proper perspective, let us first consider the position at the end of the last century. Atoms were still regarded more or less as real 'atoms', indivisible, and without an inner structure. One was mainly concerned with finding out how these atoms were arranged to form molecules and how atoms and molecules were grouped in different states of aggregation without bothering much about the nature of the forces which were responsible. Broadly speaking, a system is only influenced by a change in temperature if the energy differences associated with some possible change in the system are of the same order as its thermal energy; thus at low temperatures any temperature dependent phenomena are connected with small energy differences. Therefore it was thought that by decreasing the temperature still further one would be able to liquefy or solidify yet more gases with lower heats of evaporation or heats of melting, but that nothing unexpected would happen. Although this prospect was certainly important from the experimental point of view, it did not really produce much excitement among scientists. People busy with such activities were regarded much in the same way as someone who wanted to be first at the North Pole or run faster than anyone else. It is difficult now to realize that only a few years before the discovery of x-rays and

radioactivity and the advent of quantum and relativity theory, it was still firmly believed that there was nothing essentially new to be found out. Even scientists such as HELMHOLTZ took this view, although there was no dearth of signs that all was not well with classical theory.

The Principles of Obtaining Low Temperatures

In addition there is one other point which explained the relative indifference of scientists towards low temperature research. According to classical theory, absolute zero was not only unattainable but was without much thermodynamic significance. To understand this, let us digress to consider the principles of attaining low temperatures.^{1,2}

Fig. 1 shows the entropy of a substance as a function of temperature and a second parameter which, to fix our ideas,

we will assume to be the volume. I need hardly remind you that entropy changes are measured by summing up the amounts of heat added reversibly to a system divided by the absolute temperature at which they are added, nor that from the statistical point of view the entropy is a measure of the state of disorder. Thus, as we see in the figure, the entropy is greater for a high temperature than a low one and, in general, greater for a big volume than a small one. In order to draw up such a

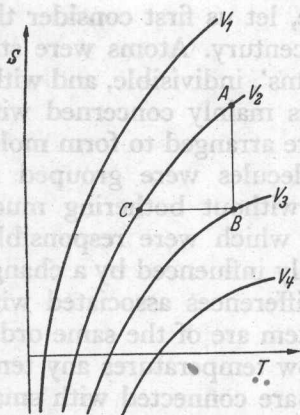


FIG. 1

Entropy of 'classical' system as a function of temperature and a second parameter V .

diagram it is necessary to know something about the specific heats. Now one of the pillars of classical physics was the law of the equipartition of energy according to which the degrees of freedom are 'counted only and not weighted'; among other things this implies that the specific heat of a solid is constant down to absolute zero. On this picture

the entropy differences between any finite temperature and the absolute zero are infinite, since

$$S_T - S_0 = \int_0^T \frac{C}{T} dT = \ln T - \ln 0 = \infty.$$

Therefore in our figure the entropy curves have to tend towards minus infinity as they approach absolute zero.

If we want to lower the temperature, the ideal way is by a reversible process and we can see from our diagram how to carry this out. We start at a finite temperature T_A and begin by changing a parameter (say the volume) from A to B in such a way that the entropy is diminished isothermally. In order to do this we have, of course, to remove a certain amount of heat equal to $T\Delta S$. We then thermally isolate the system and change the volume back to its original value, but this time we do so adiabatically. We now move along an isentropic line and reach the point C, which is at a lower temperature T_c . The total amount of disorder remains constant during the isentropic change; thus, if we increase the part due to the second parameter, that due to temperature must decrease, *i.e.* the temperature falls. This example illustrates the general principles of producing low temperatures: we must have a system at our disposal where the entropy (or the state of disorder) is strongly dependent on temperature and on a second external parameter. The simplest examples of such systems are the gases, and this is the reason why low temperatures and gas liquefaction have for a long time been nearly synonymous.

The Classical Picture

We see at once from the figure that in a classical system it is impossible to reach absolute zero, as all the entropy curves tend towards minus infinity. This unattainability of absolute zero can also be shown in another way. It is easy to derive from the diagram (Fig. 1) that the amount of work needed to cool a substance from the point A to C is $W = H_A - H_C - T_A(S_A - S_C)$. ($H = U + pV =$ enthalpy.) This means that the work needed to cool a 'classical substance' to absolute zero is infinite.

Moreover it is important to realize not only that absolute zero could not be attained but also that it was not a point of great thermodynamic interest. It was not a reference-point from which one could count *all* the quantities necessary for thermodynamic calculations, because of this infinite entropy difference.

For all these reasons, seen now perhaps with a certain amount of hindsight, low temperature research had no really wide appeal; few people thought it worth while to start work in this field with all its experimental difficulties when it did not obviously promise results of fundamental interest. Research flourished for a short period in this Institution under DEWAR, and then shifted to Leiden where KAMERLINGH ONNES kept the flag flying practically single-handed.

The Advent of Quantum Theory

The whole outlook was changed by the development of quantum theory and the discovery and interpretation of low temperature quantum effects. Perhaps the most decisive event was EINSTEIN's explanation of the falling off of the specific heats and his prediction that they would approach zero at zero temperature.³ Entropy differences between absolute zero and finite temperatures were now no longer infinite so that absolute zero could become a thermodynamic reference point. EINSTEIN's theory was later adapted to deal with systems possessing a vibrational frequency spectrum, and it was shown how to calculate the energy contents of actual crystals^{4, 5}. While in general the specific heat curves of real substances vary in a more or less complicated way, theory and experiment both show that they all tend to vanish at absolute zero.

The Third Law of Thermodynamics

Absolute zero became the thermodynamic reference point par excellence when NERNST enunciated the third law of thermodynamics,⁶ which he derived intuitively without reference to quantum theory by considering chemical equilibria at ordinary and high temperatures. This law, as

we now understand it, implies that the specific heats fall to zero, but it also postulates—and this is more important—that at absolute zero the entropy differences between all states of a system disappear. In a somewhat abbreviated way one can say that all substances at absolute zero are in a state of perfect order—a state of affairs only possible in a quantum world. While the disappearance⁸ of the specific heats alone would give rise to an entropy diagram of the form illustrated in Fig. 2a, the third law demands the form shown in Fig. 2b.

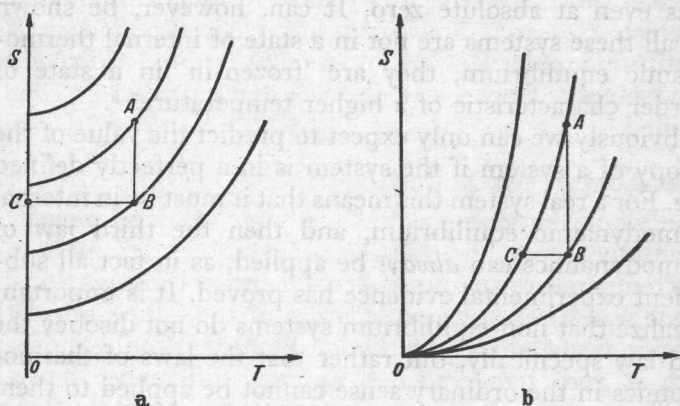


FIG. 2

Entropy of 'quantum' system, assuming (a) non-validity, (b) validity of third law.

Let us now return to the question of the possibility of reaching absolute zero. With disappearing specific heats the work necessary to cool a substance to the absolute zero is now finite and at first sight it looks as if the attainment of absolute zero would be a very easy matter. This would indeed be so, if the only consequence of introducing quantum conditions were to make the specific heats disappear; as we can see in Fig. 2a, an increase of the volume from the point B , say, would lead us directly to absolute zero. The other consequence of the third law, however, is fundamental; all the entropy curves must end up in *one* point at absolute zero (Fig. 2b). We see that, as in classical

theory, absolute zero is unattainable, but for quite different reasons and with different consequences; this is a point to which I am going to return later on.

The third law of thermodynamics is to-day the most important guiding principle in low temperature research. At first this law was not generally accepted and obvious discrepancies were pointed out; a super-cooled glass or mixed crystal, for instance, cannot be in a state of perfect order. In fact, experiments carried out on such systems and taken at their face value indicate the presence of entropy differences even at absolute zero. It can, however, be shown that all these systems are not in a state of internal thermodynamic equilibrium, they are 'frozen-in' in a state of disorder characteristic of a higher temperature^{7, 9}.

Obviously we can only expect to predict the value of the entropy of a system if the system is in a perfectly defined state. For a real system this means that it must be in internal thermodynamic equilibrium, and then the third law of thermodynamics can *always* be applied, as in fact all subsequent experimental evidence has proved. It is important to realize that non-equilibrium systems do not disobey the third law specifically, but rather that the laws of thermodynamics in the ordinary sense cannot be applied to them at all. For instance, it is not possible to speak of the vapour pressure of a glass⁷ because its internal configuration and therefore the vapour pressure depends on time—there is no point in trying to apply CLAUSIUS-CLAPEYRON's equation to it.

After a time of confusion when some authors^{10, 11} believed that the third law was sometimes valid and sometimes not, it is now generally accepted as a general law of thermodynamics and is formulated as follows:^{12, 13, 14} 'At absolute zero there are no entropy differences between any states of a system which are in internal equilibrium.' Generally a system is only 'frozen-in' with respect to one parameter and not to all, so the following version may be preferred:¹⁵ 'The contribution to the entropy of a system due to each component which is in internal equilibrium disappears at absolute zero.'

These formulations include of course the law of the unattainability of absolute zero, and it is worth while remembering that if someone thinks he has found a violation of the third law then this would imply—in principle, at least—the possibility of reaching absolute zero. Certainly he would endear himself to all low temperature physicists if he were right, but he would always find, in trying to trace the steps by which he could reach his goal, that the system with which he is concerned is actually 'frozen-in' in some state of disorder: it would be a non-thermodynamic system. The changes in the system which would be needed to reach absolute zero simply cannot be carried out; if, however, it were possible to remove the restraints, which keep the system in a non-thermodynamic state, the entropy difference at absolute zero would disappear.

At first the third law was mainly applied to the prediction of the equilibria of chemical systems at ordinary and high temperatures. This was chiefly due to the fact that NERNST was led to the law by a consideration of just such systems; but there was one other important reason. It was believed that most reaction velocities would become insignificant at low temperatures: changes of the position of the atoms in the lattice, for instance, are possible only if potential barriers can be overcome, and already at liquid air temperatures the thermal energy is small compared with the typical reaction potential barrier. All chemical activities have ceased and the little that was known about the behaviour of solids at low temperatures seemed to indicate that all other atomic processes would die away too. It is true that there were a few exceptions; the electrical resistance of metals was one of them, but even here some people believed that finally they all would become infinite. Searching for this KAMERLINGH ONNES discovered the phenomenon of superconductivity!

Zero-Point Energy

Later on many cases were found of systems in which a great deal happens at low temperatures and these are the ones on which low temperature physics now concentrates

its attention. In classical theory the motions of all the particles die out as absolute zero is approached; in quantum mechanics, however, the position is different. A zero-point energy was first introduced tentatively in PLANCK's second hypothesis;¹⁶ he assumed that the energy of an oscillator in its lowest state was $\frac{1}{2} h\nu$ (ν = the frequency of the oscillator). It was then shown that this zero-point energy must produce a difference in the vapour pressures of isotopes;¹⁷ although the available experimental evidence gave some support it was not conclusive. Further indications of the existence of this zero-point energy were given by the study of the melting point and of the law of corresponding states.¹⁸ The first quantitative proof came from the study of the intensities of x-ray diffraction patterns at low temperatures¹⁹ and later the study of the spectra of diatomic molecules²⁰ gave further confirmation. Finally, the new quantum mechanics showed the necessity of a zero-point energy, and to-day many experimental proofs exist for it.

Perhaps the simplest way to show the necessity of zero-point energy is by way of the Uncertainty Principle. If we try to determine the position of an atom very accurately, the uncertainty of its momentum increases. If one tries to fix an atom in one place by lattice forces then the atom will vibrate even at absolute zero, and the stronger the forces with which one tries to confine it (and the lower its mass) the higher the frequency of vibration and therefore the zero-point energy. A rigorous treatment of this problem leads to just the same expression for zero-point vibration as PLANCK guessed many years before; it may also be shown that other forms of motion, such as rotation, have their zero-point energy. We should note that at high temperatures (i.e. at temperatures for which kT is big compared with the energy quantum) the sum of thermal energy plus zero-point energy approaches the classical value of the energy as indicated in Fig. 3 a and b. At low temperatures, however, the total energy exceeds that of the classical system.

Zero-point energy must affect all properties of a condensed phase, but obviously only to any considerable

extent at temperatures for which kT is small in comparison to $h\nu$. Its presence will be the more important the greater $h\nu$ is in comparison with, say, the lattice energy. Thus we would not expect zero-point energy to make much difference to the properties of substances at room temperature, but its effects could become very pronounced in substances with a low boiling point. This is especially true as low-boiling substances happen to possess low atomic weights (and therefore relatively higher frequencies of oscillation).

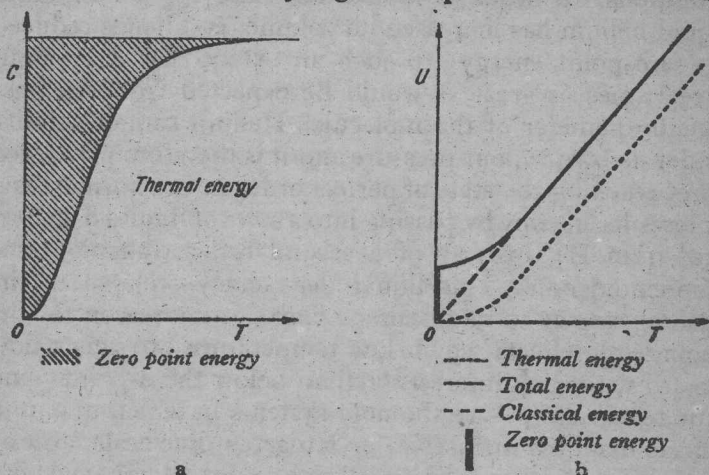


FIG. 3

Zero point energy, Thermal energy and Total energy of crystalline substance.

We find, for instance, that while the total cohesive lattice energy of solid hydrogen is of the order of 400 cal/mole, the zero-point energy counteracts about 200 cal/mole so that the measured heat of sublimation is only $400 - 200 = 200$ cal/mole. It is also worth noting that the whole of its thermal energy at the melting point amounts to only 5 cal/mole. Thus zero-point energy must play a determining role in the properties of this substance.

Liquid Helium

The most spectacular effects, however, are seen in condensed helium where about 80 per cent. of the total

'lattice' energy is counterbalanced by the zero-point energy. For the helium isotope with the mass 3 this figure is 95 per cent., which means that it comes very near to not condensing at all (although by exerting sufficient pressure any system could be brought into the state of a *crystalline order*).

The zero-point energy of a substance is decreased if its volume is increased, as this lowers the frequencies of the vibrations. In order to reduce its energy to a minimum, liquid helium has increased its volume (and hence reduced its zero-point energy), to such an extent that it is about three times as great as would be expected from the gas-kinetic diameter of the molecule. Helium cannot solidify under its own vapour pressure and it is therefore prevented from reaching the state of perfect order in the normal way. It loses its entropy by passing into a state of 'liquid degeneracy', (He II), by way of a second order transition, the ' λ -phenomenon'. This liquid degeneracy—related to the gas degeneracy to be discussed later—is the reason for the remarkable effects which low temperature physicists now regard with such interest. Helium below the λ -point—and superconductors—are the only systems in which quantum effects manifest themselves on a macroscopic scale, at least under terrestrial conditions. Professor ALLEN will deal with these effects in a later lecture, and also say something about recent experiments made using ^3He which not only exhibits a much higher zero-point energy but also follows a different statistics.

Electrons in Metals

Zero-point energy is also of fundamental importance when we come to deal with the properties of electrons in metals. In pre-quantum times a great number of these properties had been explained successfully by the assumption of a free electron 'gas', but this involved two major difficulties. Firstly, the specific heat of a metal should have included a contribution from the electron gas of $\frac{3}{2}R$, while the measured values gave no sign of this additional contribution. Then in order to explain the values of the electrical and thermal

conductivity, one had to assume that the electrons had a random velocity which was constant and independent of temperature.

At first, quantum theory was only applied to vibrations and rotations and not to the translational motion of the atoms of a gas. NERNST, when he first put forward his theorem, only postulated it for condensed phases, but he soon extended it to include gases, not because of any particular theory, but because he felt that if his theorem were a general law of Nature, it should include all phases. He therefore postulated that a state of 'gas degeneracy'^{21, 6} should set in at low temperatures and high densities.

The development of quantum theory finally led to a confirmation of NERNST's inspired guess and gave the quantum statistical explanation for it. It was shown that the specific heat of an ideal gas would have to approach zero with falling temperature and that there should be deviations from the ideal gas law given by the two following equations:

$$pV/RT = 1 - 0.318A \quad (\text{BOSE-EINSTEIN}) \quad \text{or}$$

$$pV/RT = 1 + 0.176A \quad (\text{FERMI-DIRAC})$$

The first formula is for a gas which follows BOSE-EINSTEIN statistics, the second for one following FERMI-DIRAC statistics corresponding to symmetry or anti-symmetry of the wave functions. (*A*) represents the degeneracy parameter:

$$A = \frac{Nh^3}{V(2\pi mkT)^{3/2}}$$

N = AVOGADRO's number,

h = PLANCK's constant,

k = BOLTZMANN's constant,

m = mass of particle.

Thus the lower the temperature and the smaller the molar volume and the mass of the particles, the greater the deviations from the ideal gas law. These results could not be verified experimentally with ordinary gases, because at temperatures and volumes where the deviations would be measurable the gases would have condensed. Also there is no hope of detecting the degeneracy of a gas just by trying to reduce the temperature, even to the new region below 1°; the effect of the falling vapour pressure (and hence an increasing molar volume) much outweighs that of the falling

temperature. For instance, in saturated helium at 4.2° the deviations would be 4×10^{-3} ; at 2° , 6×10^{-4} ; at 1° , 10^{-5} , and at 0.5° , 10^{-9} . The value at 4.2° should still be observable but is completely overshadowed by the much bigger deviations due to the non-ideality of the gas.

When we consider the behaviour of electrons in metals the position is quite different. Owing to the particular structure of a metal we have a very high density of electrons and in addition the mass of the electron is very small. This combination has the effect that the electron gas begins to

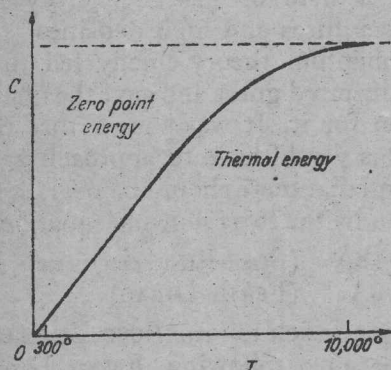


FIG. 4

Sketch of specific heat of the electron gas in a metal.

become degenerate at very high temperatures, of the order of $10,000^\circ$ (Fig. 4). Thus at room temperature, for instance, the electron gas is practically completely degenerate and no considerable contribution to the specific heat can be expected. The detailed calculation shows that finally the specific heat of the electron gas, obeying the FERMİ-DİRAC statistics,

falls towards zero proportionally to the absolute temperature. This has been confirmed by experiments at very low temperatures, where the specific heat of the metal lattice has virtually disappeared and it is thus possible to detect the extremely small contribution of the electrons. The high degeneracy temperature also implies that the electrons have a very big zero-point energy and this explains why they have a constant random velocity.

Electrical Conductivity

The most interesting branch of electron metal-physics is that of the 'transport phenomena', particularly electrical conductivity. On classical theory it is certainly to be expected

that the resistance of a metal should fall with reduction of temperature, since the atoms vibrate less strongly in the lattice, but it was the advent of quantum theory which made it possible to understand the remarkable increase of conductivity at low temperatures. The theory shows that a mathematically perfect metal crystal should have no electrical resistance at absolute zero, though the presence of impurities and lattice defects in real metals seems to keep their resistances finite. It is generally found that the resistance tends to a limiting value which may be as little as 1 part in 10^4 of the room-temperature resistance.

There is, however, one very remarkable exception to this general rule, the phenomenon of superconductivity, which was first observed by KAMERLINGH ONNES in 1911. In certain metals and compounds the resistance falls abruptly to zero at a finite temperature; there is as yet no full explanation of this effect. It is true that the phenomenological theory of the LONDONS²² has led to a great clarification of the position, but of course not to an explanation of the underlying mechanism. In the last year, however, the theories of FRÖHLICH and BARDEEN seem to have given the first pointers towards an understanding. Dr. MENDELSSOHN is going to deal in his lecture with this remarkable phenomenon.

Apart from superconductivity there are several other phenomena of great interest, for example the influence of a magnetic field on electrical (as well as on thermal) resistance. I would also like to mention the recently discovered fact that in some substances the electrical resistance shows a minimum and begins to rise again at the lowest temperatures. This is very puzzling and no explanation has yet been given.

Magnetic Phenomena

A third subject of great interest to low temperature physicists will be among the subjects discussed in Dr. KURTI's lecture; it is the study of paramagnetism at very low temperatures, which among other things has led to a very considerable extension of the temperature range